

Quarterly Progress Report (Field Office Project Template)

Project Title: Photo-catalysts for Solar Energy and Hydrogen Production

Award Number: [Official Award Number per the agreement]

Recipient:

Project Location: University of Louisville, Louisville KY

Reporting Period: January 1, 2006 to September 30, 2007

Date of Report: January 11, 2007

Written by: Gerold Willing

IMPORTANT NOTE: If any part of your quarterly report contains **proprietary/confidential information**, or details that should not be released to the general public, the specific sections of the report should be marked as such, by clearly marking the beginning and end of the confidential information. The marked sections will not be released to the general public or any unauthorized parties.

Status:

Task number: 1. Develop “tree-like” nanoscale structures with a gradient material composition for efficient charge transfer and light harvesting utilizing a novel catalyst free, low temperature synthesis technique.

- Planned Activities:** Study the growth mechanisms of nanowire and the “tree-like” structures with emphasis on growth direction, bandgap and work function. Solar cells utilizing these materials will be investigated with respect to their overall efficiency and durability.
- Actual Accomplishments:** During the course of this project, it became obvious that new methods of fabricating nanowires on the bulk scale would be needed to meet not only the immediate research needs, but also the longer term commercialization needs. Towards this end, we demonstrated the synthesis of bulk quantities of various metal oxide nanowires (NWs) using the microwave plasma jet reactor: (a) ZnO (b) SnO₂ (c) Cu doped ZnO NWs (4 at% Cu) (d) TiO₂. All these powders are analyzed using SEM, TEM and Raman and XRD techniques to confirm their phase and crystallinity. Unfortunately, particle deposition on quartz tube walls is a concern for continuous production of bulk powders. We are currently designing a larger quartz tube to reduce the wall deposition. Two gram quantities of ZnO NWs have successfully been produced for demo purposes. A provisional patent application has been filed by UofL to protect the above reactor and the process (S/N 60/978,673). Based on these materials, we have shown that the SnO₂ NWs based DSCs yield open circuit voltages of 560mV compared to 360 mV by nanoparticle based cells. Additionally, SnO₂ NWs coated with TiO₂ particles produced the highest efficiency (>4%) compared to either SnO₂ NWs or SnO₂ nanoparticle based cells. Work on composite structures, which will lead to a fuller development of the “tree-like” structures, has involved decorating nanowires with nanoparticles. To date these structures show about 3% efficiency (8.5 mA/cm², 0.7 V) at 1 sun. These results were obtained using SnO₂ nanowire mat electrodes treated with

Titanium Oxide nanoparticles using solution chemistry. The same sample without this treatment yielded about 1.5 % efficiency (6 mA/cm^2 , cell voltage of 0.55 V).

3. **Explanation of Variance:** The slight change in direction to include bulk production of nanowires was necessitated by the need for materials during the research and testing phase. Without a significant supply of nanomaterials, it would be impossible to conduct research into the development of these nanoscale photo-catalysts in a reasonable time frame. The new reactor design developed under this program gives UofL a unique and important capability within this research area.
4. **Plans for Next Quarter:** NA

Task number: 2. Investigate the role of surface and bulk processes involved in photoelectrode performance utilizing Atomic Layer Deposition.

1. **Planned Activities:** Tailor titanium oxide photoelectrode materials in a controlled and graded manner by using a dopant metal precursor or NH_3 reactant for selected cycles during film deposition to separately investigate and enhance each step of the photoelectrochemical process
2. **Actual Accomplishments:** Initial work focused on utilizing zirconium as a dopant to the TiO_2 films for modifying the band structure and current production in a photoelectrochemical cell. These films showed an enhancement in photocatalytic activity. Additionally, we used ALD TiO_2 coating on SnO_2 NWs and found out that they do not increase in efficiency. This is in contrast to the results discussed in Task number 1 where TiO_2 nanoparticles deposited on the SnO_2 NWs do increase efficiency. These results suggest that the 3 phase line interface between the nanoparticles, the NWs and the electrolyte solution plays a role in either the charge transfer or charge generation processes. An additional explanation may relate to an increase in overall surface area on the nanowire in the case of the nanoparticles as opposed to the contiguous thin film coating.
3. **Explanation of Variance:** None
4. **Plans for Next Quarter:** NA

Task number: 3. Determine the fundamental mechanisms involved in charge separation and mobility within photochemical system using transient absorption spectroscopy and electrochemical atomic force microscopy (EC AFM).

1. **Planned Activities:** Utilize EC-AFM and transient absorption spectroscopy to identify how the charging behavior changes on a single particle with changes in particle size and amount of charge transferred, how charge is transferred from the one system component (semiconductor, metal nanoparticle, dye molecule) to another and determine what role the interfacial regions between the system components play in charge transfer mechanism, especially in the presence of linking molecules.
2. **Actual Accomplishments:** Of the three sub-projects, this one required the largest commitment in terms of building up of the infrastructure to accomplish the long terms goals and planned activities. The initial focus was dedicated to identifying the individual components needed for the EC-AFM. Once the vendors were identified and the

components ordered, work proceeded with assembly and integration of the two systems. This was completed in March of 2007. Training and experimental work began in spring of 2007. Sample preparation was identified as a key early step to the process as it became obvious that a full nanowire mat would not be easily imaged within the AFM. Work shifted to developing the NW mats on ITO to ensure that imaging in a fluid state can proceed. NWs are bound to the ITO surface through weak van der Waals forces, resulting in movement of the NW mat across the ITO surface during AFM imaging in fluid. This has forced us to sinter the films prior to AFM imaging which eliminates the possibility of testing the un-sintered wires in a fluid phase without some other means of dye attachment. The sintering process may alter the surface in such a way as to partially inhibit the attachment of dye molecules to the NW surface, as has been discussed in prior reports. We are currently reviewing the DSC assembly process and adjusting process variables such as sintering temperature and time, mat thickness, dye concentration and diffusion time in an effort to enhance dye adhesion to the NW surface. Additional work also focused on the dye attachment as it has been observed through the recent AFM studies that the dye molecules are not uniformly attached onto the NW surface. This is currently being linked to a subtle variation in NW surface chemistry, most likely arising from a change of the exposed metal or oxygen atoms on the NW surface. Additional work is being focused on modification of the NW surface to ensure a consistent surface chemistry which should enable even dye adsorption across the NW surface.

3. **Explanation of Variance:** Identification of components for the EC-AFM and assembly took far longer than initially expected due to personnel changes part way through the project. Once assembly was completed, focus shifted to proper substrate preparation for the techniques being utilized in this investigation. During the course of technique development, additional preparation issues relating to the dye adsorption were discovered. Since the full characterization is dependent upon a consistent dye coverage of the nanowire, it was necessary to shift our focus to dye adhesion and the role of the interface between the dye molecule and the nanowire surface.

4. **Plans for Next Quarter:** NA

Patents:

M.K. Sunkara, J.H. Kim and V. Kumar, "Reactor and Method for Production of Nanowires", US Provisional Patent Application Filed, 60/978,673, October (2007).

Publications / Presentations:

Suresh Gubbala, Vivekanand Kumar, Uros Cvelbar, Mahendra K. Sunkara, *Tin Oxide And Niobium Pentoxide Nanowire Based Dye Sensitized Solar Cells*, to be presented at the **2007 AIChE Annual Meeting**, Salt Lake City, UT, November 4-9, 2007.

Vivekanand Kumar, Jeong H. Kim, Boris D. Chernomordik, Mahendra K. Sunkara, *Bulk Production of Metal Oxide Nanowires Using A Novel Microwave Plasma Reactor*, to be presented at the **2007 AIChE Annual Meeting**, Salt Lake City, UT, November 4-9, 2007.

Sudhira Pasupuleti and Gerold A. Willing, *Investigating the Nanoscale Charge Mobility for Increasing the Efficiency of Photoelectrochemical Cells*, to be presented at the **2007 AIChE Annual Meeting**, Salt Lake City, UT, November 4-9, 2007.

S. Gubbala, V. Chakrapani, V. Kumar, and M. K. Sunkara, *Band-edge engineered hybrid structures for dye sensitized solar cells based on SnO₂ nanowires*, Submitted to Nano Letters (2007).

Suresh Gubbala, Jyothish Thangala and Mahendra K. Sunkara, *Nanowire Based Electrochromic Devices*, **Solar Energy Materials and Solar Cells**, 91(9), 813-820 (2007).

Suresh Gubbala, Sreeram Vaddiraju, Jyothish Thangala, Biswapriya Deb, Mahendra K. Sunkara, *Nanowire Based Dye Sensitized Solar Cells and Electrochromic Devices*, presented at the **2006 AIChE Annual Meeting**, San Francisco, CA, November 12-17, 2006.

Shenghong Qiu, Thomas L. Starr, *Modified Titania Films for Photoelectrochemical Applications*, presented at the **2006 AIChE Annual Meeting**, San Francisco, CA, November 12-17, 2006.